

Quantum size effects in simple colored glass

J. Warnock and D. D. Awschalom

IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

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Finite size effects have been observed at low temperatures for electrons confined to semiconductor microcrystallites embedded in a simple borosilicate glass. Luminescence data reveal large electronic energy shifts relative to bulk energy levels which can be used to calculate the confinement energy of the localized electrons. This system provides an attractive alternative to quantum well heterostructures, permitting direct optical studies of electron confinement effects over a wide range of temperatures.

An electron confined to some region in space is analogous to a quantum mechanical particle in a box, and the experimental problems associated with the real observation of such imprisoned electrons have recently been receiving considerable attention. In particular, the effective electron mass in a semiconductor is often much smaller than a free electron mass, thus increasing the magnitude of any expected localization effects. Here we report the observations of quantum size effects due to electron and hole confinement in tiny Cd(S,Se) microcrystallites embedded in glass. The glass provides a deep confining potential, thereby ensuring that the excitations are in true "boxlike" states. Moreover, the glasses are mechanically stable, can easily be cooled to low temperatures, and are commercially available¹ in the form of ordinary colored glass filters.

It has previously been shown² that glass filters contain many small crystallites of Cd(S,Se), the optical manufacturers using very pure batch materials in order to achieve the desired shape cutoffs. We have selected two filters, Corning No. 2-61 and No. 2-59, whose crystallites have band gaps of order 2.0–2.1 eV, giving them a deep red color. These samples were chosen such that their crystallite chemical compositions were ostensibly the same in each of the two glasses. Transmission electron microscope photographs taken of each filter showed the crystallite size distribution to be quite uniform with diameters of approximately 94 and 106 Å, respectively. Moreover, a few distinct islands of bulk material could be seen clearly. Microprobe analysis indicated that all the crystal compositions were, in fact, identical and given by $\text{CdS}_{0.27}\text{Se}_{0.73}$.

These glasses are colorless when made by the usual glassmaking process³ and obtain their color only after reheating. When the glass is annealed, the crystallite thickness increases through Ostwald ripening⁴ in a manner similar to that observed in thin film coalescence. Hence the crystallite size in these doped glasses can be readily controlled via the annealing time and temperature, thereby determining the electron confinement energy. This allows the detailed observation of the evolution from the electronic behavior in the tiny microcrystallites to that in the bulk, as confinement effects are expected to vanish for crystal sizes greater than a few hundred angstroms. In addition, the process of Ostwald ripening itself may be readily studied.

We have observed the effects due to electron confinement in these small microcrystallites using luminescence spectroscopy. The spectra were obtained using a tunable dye laser in order to excite excitons in the system. The excitation energy was set above the absorption edge of the

glass filters and the transmitted luminescence focused onto the slit of a 0.64-m single-pass monochromator. The filters themselves sat in a variable-temperature optical cryostat, the temperature of which could be varied from 1.2 K to room temperature. The low temperature luminescence spectra of the two different glasses are shown in Fig. 1.

We attribute the dominant peak (*Q*) to bound excitonic recombination in the microcrystallites, whereas the smaller

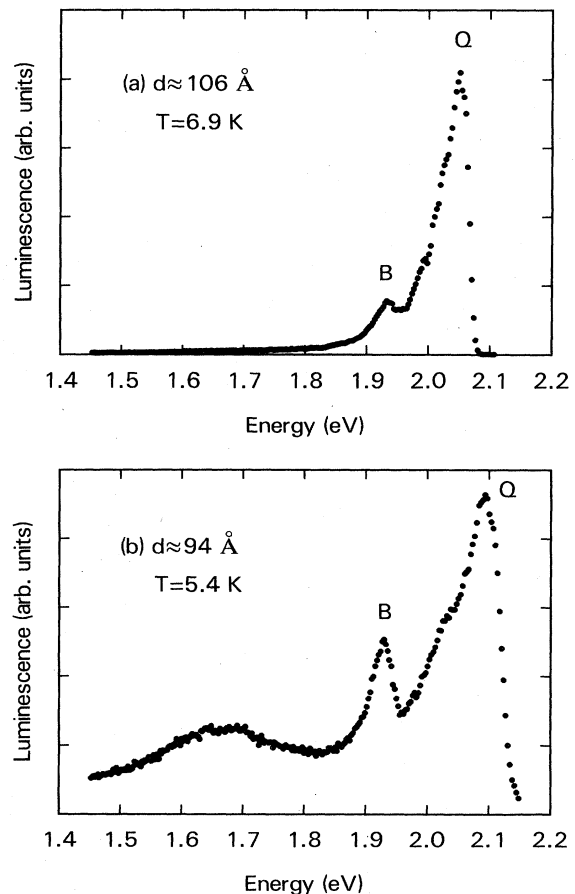


FIG. 1. (a) Low temperature luminescence spectrum from Corning Glass optical filter 2-59. Peaks *Q* and *B* label the microcrystallite and bulk luminescence, respectively. The crystallite size *d* was measured from the transmission electron microscopy negatives. (b) Same as (a), but for filter 2-61.

peak at lower energy (*B*) arises from recombination in the larger bulklike fragments and hence has the same energy in both spectra. The energy of the bulk peak matches, within our resolution, that predicted from the chemical analysis and the known variation of the band gap with composition.⁵ In this case the differences in the optical absorption edges and the feature (*Q*) in the luminescence spectra of the two glass samples are entirely due to shifts in the electronic energy levels as a result of the differing confinement energies in the two different sizes of crystallites.

The energy difference between the two luminescence peaks (*Q*) and (*B*) provides an experimental measure of the confinement energy E_c , from which one can extract an estimate of the crystallite size. A relation between the confinement energy and the crystallite size may be obtained to first order by assuming that the excitons are trapped in spherical volumes of diameter d .⁶ This may be expressed as

$$E_c = (2\hbar^2\pi^2/\mu d^2) - (3.6e^2/\epsilon d),$$

where \hbar is Planck's constant, μ the reduced mass of the exciton, and ϵ the dielectric constant. The first term is simply the kinetic energy of the confined exciton, and the second represents the Coulomb interaction of the electron with the hole.

From the measured composition of the microcrystallites and a linear interpolation between the known values⁷ for

CdS and CdSe, we find that $\epsilon = 8.8$ and $\mu = 0.11m_0$, m_0 being the free electron mass. From Fig. 1 we see that $E_c = 0.122$ eV for the glass with the larger crystallites, yielding a size $d = 84$ Å. For the second sample, $E_c = 0.169$ eV, giving $d = 74$ Å. The reasonable agreement between the above values and the measured crystallites provides further evidence that the observed luminescence energy shifts are due to confinement effects. Note that similar localization behavior has been observed in various semiconductor layered heterostructures,⁸ and, more recently, in small crystals in colloidal solutions.⁹

Next we discuss the broad feature centered about 1.7 eV, seen in Fig. 1(b). This feature is much more pronounced in the glass with the smaller crystallites and becomes even stronger as the temperature is increased (Fig. 2). The luminescence is at lower energy than the donor-acceptor pair recombination observed in bulk Cd(S,Se) (Ref. 5) and extends into the low energy region of the spectrum. This peak is most likely due to surface-related defects, and therefore is stronger in the glass with smaller crystallites.

As the temperature is increased from 10 K, the appearance of the luminescence from the defect band is accompanied by a large relative decrease in the intensity of the higher energy excitonic peaks (*Q* and *B*). The temperature dependence of the intensity of these peaks in one of the glasses is shown in Fig. 3. The fact that the two peaks show

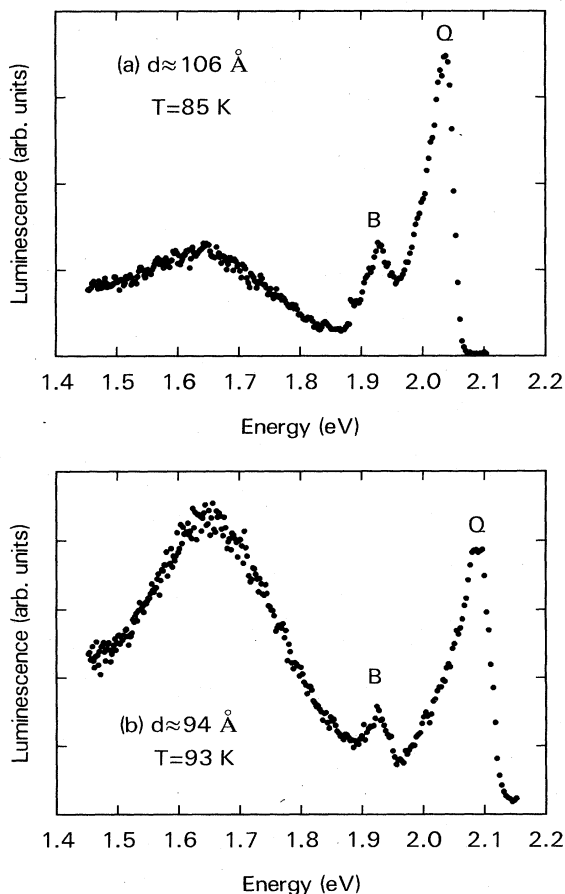


FIG. 2. (a) High temperature luminescence spectrum from Corning Glass optical filter 2-59. (b) Same as (a), but for filter 2-61.

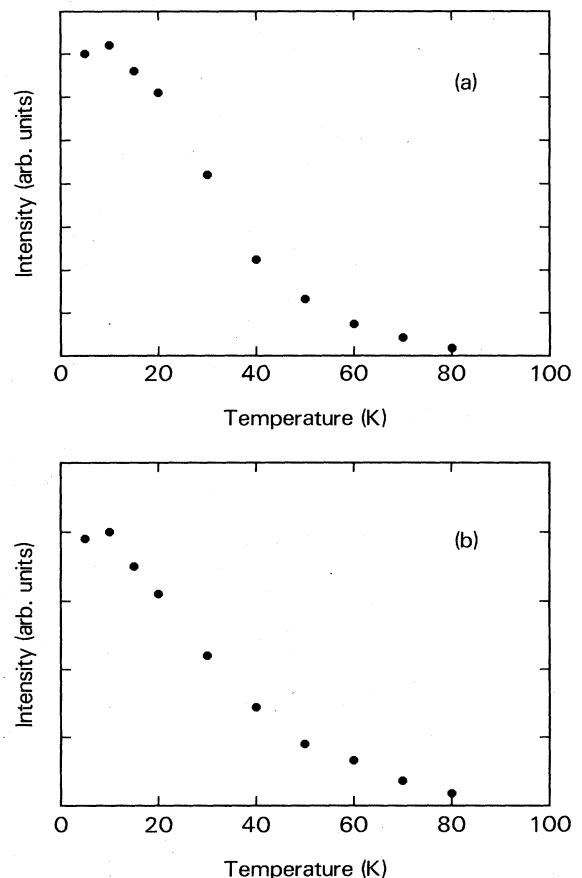


FIG. 3. (a) Temperature dependence of the microcrystallite luminescence (*Q*) from Corning Glass filter 2-59. (b) Temperature dependence of the bulk luminescence (*B*) from the same filter.

qualitatively similar temperature dependences attests to the fact that both are associated with bound excitonic recombination as described above. The different temperature dependence of the defect band is understandable, since the energy of these surface states is further from the band edge than that of the excitonic states. Thus, as the temperature increases, the relative populations of the two types of states will change. The data indicate that the population of the lower energy surface defect levels increases with temperature as carriers are thermally excited out of the higher energy excitonic states. As the defect luminescence becomes visible at temperatures above ≈ 45 K, its appearance is clearly related to the decrease in the intensity of the excitonic luminescence. A detailed investigation of the defect band recombination would be useful in the study of surface states and the way in which they effect the electron-hole recombination (see Ref. 10). An important advantage of working with these microcrystallites is that their surface area to volume ratio is large, thus greatly enhancing surface effects such as degenerate four-wave mixing.^{2,11}

In summary, we have shown that direct optical methods may be used to explore the properties of microcrystallites in simple glass. This particular system has revealed the ex-

istence of finite size effects, where electrons trapped in tiny crystals show the effects of quantum confinement. Commercial optical filter glasses are a convenient host in which to study microcrystallite excitations over a wide range of temperatures, and are potentially useful in the investigation of many different physical problems. As a simple alternative to sophisticated quantum well heterostructures, these microcrystallites in glass provide the opportunity of elegant experimental measurements. By annealing these glasses for variable periods of time, one should be able to observe the transition from size-constrained behavior to that of the bulk and, furthermore, can also study surface states and their role in electron-hole recombination. In addition, at the proper concentration it should be possible to witness collective behavior and tunneling between crystallites. Finally, time-resolved optical measurements should be performed in order to probe the dynamical aspects of these various phenomena.

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¹Corning Glass Works, Industrial Materials Dept., Corning, NY 14830; Kopp Glass, Swissvale, Pittsburgh, PA 15218.

²R. K. Jain and R. C. Lind, *J. Opt. Soc. Am.* **73**, 647 (1983).

³L. A. Provenzano (private communications).

⁴B. K. Chakraverty, in *Crystal Growth: An Introduction*, edited by P. Hartman (North-Holland, New York, 1973), p. 86.

⁵D. W. Langer, Y. S. Park, and R. N. Euwema, *Phys. Rev.* **152**, 788 (1966).

⁶L. E. Brus, *J. Chem. Phys.* **80**, 4403 (1984).

⁷B. Segall and D. T. F. Marple, in *Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J. S. Prener (North-Holland, New York, 1967), p. 344.

⁸R. Dingle, W. Wiegmann, and C. H. Henry, *Phys. Rev. Lett.* **33**, 827 (1974).

⁹R. Rossettii, J. L. Ellison, J. M. Gibson, and L. E. Brus, *J. Chem. Phys.* **80**, 4464 (1984).

¹⁰R. Rossettii and L. E. Brus, *J. Phys. Chem.* **86**, 4470 (1982).

¹¹S. S. Yao *et al.*, *Appl. Phys. Lett.* **46**, 801 (1985).